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Mössbauer study of biofilms formed along a canal of the Gellért Hill, Buda Thermal Karst, Hungary

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Abstract Biofilm samples, formed within 6 weeks, collected from different distances (1, 8, 20, 40, 60, 80, 100, 120 m) from the outflow of thermal water along an artificial canal, Gellért Hill, Buda Thermal Karst, Hungary, were investigated by ^{57}Fe Mössbauer spectroscopy, SEM, XRD and other analytical methods. 78 K Mössbauer spectra of all lyophilized samples showed a doublet, which can be associated with ferrihydrite and/or superparamagnetic goethite produced by the bacteria being present in the thermal water. An abrupt decrease of normalized spectral area was observed with increasing distance of location of samples from the outflow. This indicates the decrease of iron content of samples along the distance from the outflow. ^{57}Fe Mössbauer spectroscopy was able to detect bacterial biofilms formed after 6 weeks.

Keywords ^{57}Fe Mössbauer spectroscopy · Biofilms collected in a stream canal · Buda Thermal Karst · Gellért Hill

1 Introduction

The Buda Thermal Karst (BTK) area is in focus of research interest because of thermal water resources as well as ongoing hypogenic karstification processes [1]. The interaction of the rocks with water resulted in the formation of complicated network of caves here. A possible biofilm assisted evolution of these caves occurs since flowing water can provide a

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permanent transport of dissolved solids with special elementary composition and nutrients for evolutions of biofilms [2–4]. In previous works [5] we have found that the main iron-bearing phases in the biofilms are ferrihydrite and goethite in the spring caves of Buda Thermal Karst, by the help of ^{57}Fe Mössbauer spectroscopy. In work [5], the long period development of biofilms under natural conditions at the springs were studied. In the present work, however, an in-situ experimental study was carried out for the understanding of the evolution of bacterial biofilms as a function of thermal water flow kinetics along an artificial canal, Gellért Hill, BTK. Sterile glass slides, serving as precipitation surface, were placed at different distances (1–120 m) from the outflow.

2 Experimental

The samples were collected from different distances (1, 8, 20, 40, 60, 80, 100, 120 m) from the outflow of a thermal spring along an artificial canal, Gellért Hill, BTK, Hungary, 6 weeks after the steril glass slides had been placed.

The ^{57}Fe Mössbauer measurements of lyophilized samples were carried out with a conventional constant acceleration (WISSEL) Mössbauer spectrometer using integrated multichannel analyzer and scintillation detection in transmission geometry. The samples were measured at 78 K temperature by means of a JANIS liquid helium cryostat. A ^{57}Co source of 0.8 GBq activity in Rh matrix supplied the gamma rays. The isomer shift values are given relatively to α-iron at room temperature. The analysis of the Mössbauer spectra was carried out with the MOSSWINN 4.0 code [6]. The precipitates were additionally characterized by light microscopy, SEM and XRD, too. The details of these results will be published later on elsewhere.

3 Results and discussion

The temperature, pH, electrical conductivity and concentration of Ca^{2+} and HCO_3^- of the water were measured, showing stable values at the outflowing point which represented the discharging regional groundwater flow system [1, 3, 4].

^{57}Fe Mössbauer spectra, recorded at 78 K, of lyophilized biofilms collected in the canal in different distances from the outflow are shown in the Fig. 1. All spectra exhibited a doublet envelope. The Mössbauer parameters are depicted in the Table 1.

Neither Fe^{II} and nor magnetically split spectra were detected. The doublet can be associated with ferrihydrite and/or superparamagnetic goethite based on our earlier Mössbauer study [5] performed with biofilms originated from the BTK region. This new study demonstrated the capability of bacteria to induce precipitation of such a Fe^{III} phases after a time as short as 6 weeks (Fig. 1, Table 1). Nevertheless, this short period was probable not enough to develop siderite which was also found earlier [5] as a minor phase.

It was found that the spectral area normalized to the background decreased with the distance of location of samples from the outflow of the water (Fig. 2). This is associated with the decrease in iron content of the precipitates along the increasing distance. A drop in the quadrupole splitting seems to appear around 20 m which may indicate some changes associated with the size or defect structure of the evolving ferrihydrite (or superparamagnetic goethite) crystallites as produced by the bacteria. Note, however, that the iron content is so low in the biofilms, that even the sample with highest iron concentration (originated from 1 m distance) is undetectable without lyophilization, which can have an effect on the crystal

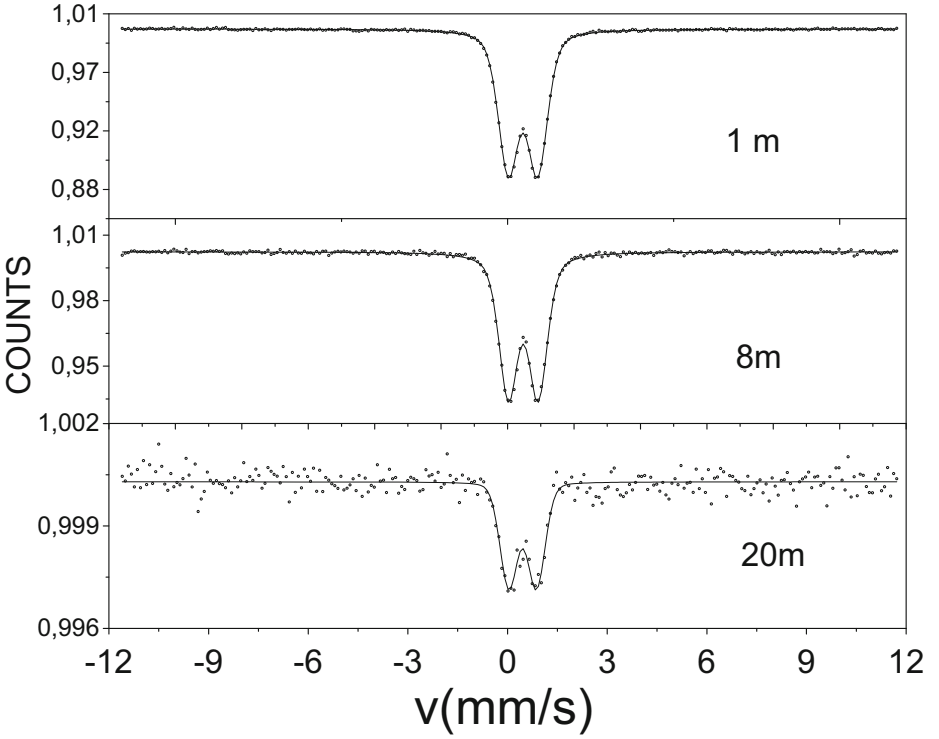

Fig. 1 ^{57}Fe Mössbauer spectra, recorded at 78 K, of lyophilized biofilms collected in the canal in different distances from the outflow, indicated in the spectra

Table 1 78 K Mössbauer parameters of lyophilized biofilms collected in the canal in different distances from the outflow

Sample distance from the outflow	1 m	8 m	20 m	40 m	60 m	80 m	120 m
Parameters							
A (%)	11.3	6.5	0.4	0.2	0.18	0.15	0.14
rel. to back-ground							
δ (mm/s)	0.47	0.46	0.45	0.42	0.4	0.46	0.43
	(0.001)	(0.000)	(0.014)	(0.047)	(0.069)	(0.073)	(0.093)
Δ (mm/s)	0.89	0.88	0.82	0.60	0.63	0.59	0.55
	(0.002)	(0.00)	(0.022)	(0.067)	(0.077)	(0.088)	(0.16)
W (mm/s)	0.48	0.53	0.57	0.42	0.50	0.64	0.65
	(0.011)	(0.004)	(0.089)	(0.12)	(0.19)	(0.25)	(0.32)

morphology. The microscopy, SEM and XRD results are consistent with the Mössbauer results and show the change in character of precipitates at distances higher than 20 m, when the chemical precipitation of crystalline calcite phases became more meaningful. The velocity of flowing water may have a significant impact on the formation of Fe(III) phases as well.

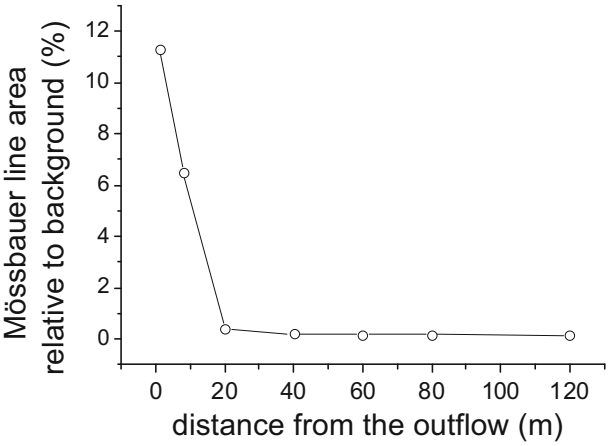

Fig. 2 The Mössbauer line area relative to background as a function of the sample's distance from the outflow

4 Conclusion

Fast evolving precipitates were observed in an artificial canal at the Gellért Hill, Buda Thermal Karst, Hungary, where an outflow of thermal water were experimentally studied. ^{57}Fe Mössbauer spectroscopy was able to detect bacterial biofilms formed after 6 weeks, associated with ferrihydrite and/or superparamagnetic goethite phases. The Mössbauer spectral area decreased considerable with the distance from the outflow, reflecting the considerably decrease of iron content of biofilms with the distance. There is a change in the character of the precipitates at around 20 m distance from the outflow.

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